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POTASSIUM IN PACIFIC KELPS AND IN
ROCKS OF DIFFERENT GEOLOGIC AGE

A DISSERTATION SUBMITTED TO THE
FACULTY OF THE DIVISION OF THE
PHYSICAL SCIENCES IN CANDIDACY FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS
AND
DEPARTMENT OF GEOLOGY AND PALEONTOLOGY

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The Relative Abundance of the Isotopes of Potassium in Pacific Kelps and in Rocks of Different Geologic Age

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The Dempster double focusing mass spectrograph has been used to determine the K^{39}/K^{41} isotope ratio in certain Pacific kelps, fossils, and rocks of different geologic age. Within the 1 percent accuracy obtainable, the potassium isotope ratio for the kelps and two Upper Cambrian fossils examined is the same as that of rocks. Rocks whose ages vary from Early pre-Cambrian to Tertiary show no measurable difference in the potassium isotope ratio, within 1 percent error. The average value of the potassium isotope ratio was found to be 14.12 ± 0.28 . Fluctuations in the ratio are attributed to isotope effects of the hot-filament ion source.

INTRODUCTION

DURING the past seven years there have been reported variations in the relative abundance of the stable isotopes of three elements. Variations in the relative abundance of the stable isotopes of oxygen were found by Dole¹ in his careful measurements of the density of water in different localities. Variations of 5 percent in the isotope ratio of the stable isotopes of carbon (C^{12}/C^{13}) have been observed by Nier² and his collaborators.³ Variations of as much as

15 percent in the ratio of the relative abundance of the stable isotopes of potassium (K^{39}/K^{41}) have been reported by Brewer.⁴ As emphasized by Brewer, variations of this order of magnitude are too small to be detected by any of the present chemical techniques of measuring atomic weights of the above elements. Therefore, more precise determinations, such as those obtainable with the modern mass spectrograph or by careful density measurements, must ordinarily be employed.

It seemed desirable to have the above observations substantiated and supplemented by further studies. Goodman⁵ has already pointed out the

¹ M. Dole, J. Chem. Phys. **4**, 268, 778 (1936).

² A. O. Nier and E. A. Gulbransen, J. Am. Chem. Soc. **61**, 697 (1939).

³ B. F. Murphy and A. O. Nier, Phys. Rev. **59**, 771 (1941).

⁴ A. K. Brewer, J. Am. Chem. Soc. **58**, 365 (1936).

⁵ C. Goodman, J. App. Phys. **13**, 276 (1942).

importance of carrying on such studies of the isotopes of potassium because of its widespread occurrence on the earth's crust (2.5 percent of the earth's crust and the seventh most abundant element) as well as its importance in essentially all biological processes.

The present paper contains measurements of the relative abundance of the potassium isotopes in certain potassium-bearing plants and rocks and observations of the ratio in rocks of different geologic age.

EXPERIMENTAL DETAILS

I. The Ion Source

The use of a hot filament as a source of alkali ions has been a standard practice for many years in mass spectrograph work. Recently it has been demonstrated by Blewett and Jones⁶ that aluminosilicates of the alkali metals are the best thermionic sources of ions yet tried and that ternary compounds of alkali oxide, alumina, and silica are, in general, better emitters of the alkali ions than binary compounds. They further noted that the synthetic aluminosilicates of each of the five alkali metals of composition $R_2O \cdot Al_2O_3 \cdot 2SiO_2$ are ion-emitters and are as good as, or in some ways superior to, the natural minerals (spodumene, jadeite, leucite, pollucite) which have ordinarily been used in the past.

Throughout the course of the present work potassium aluminosilicates were used. The potassium aluminosilicate to be studied was powdered and mounted on a filament of 0.0005-inch-thick platinum (plus 10 percent iridium) foil cut in the form of a strip 15 mm by 1 mm. Distilled water was used as a binder. Enough powder was always used so that, after fusion, a thin layer of glass completely covered the platinum strip throughout about 6 mm of its central portion. Before putting on the powder each platinum strip was heated at white heat for a few minutes to drive off any volatile potassium impurities incorporated in the platinum foil. Brewer noted that most commercial platinum has some potassium impurities in it.⁷ To ascertain that the technique of pre-heating the filaments was effective, a clean platinum strip was once put into

the apparatus after pre-heating; it was found that no detectable potassium ions were emitted even near the melting point of the platinum.

The composition of the aluminosilicates used in the present investigation varied with the particular material under examination. In the case of the modern plants under study, their ash was combined with alumina and silica to make artificial potassium aluminosilicates. Details of the technique for this will be described below. In the case of the rocks under study, the investigation was confined chiefly to those igneous rocks containing one or more of the following natural minerals: orthoclase ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$); microcline ($K_2O \cdot Al_2O_3 \cdot 6SiO_2$); muscovite ($2H_2O \cdot K_2O \cdot 3Al_2O_3 \cdot 6SiO_2$); perthite (a mixture of orthoclase and albite [$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$]); microcline-perthite (a mixture of microcline and albite). It will be noted that all of these minerals are potassium-bearing aluminosilicates. That these minerals, when heated, are good emitters of potassium ions was discovered during the preliminary experiments incident to the present investigation.⁸ All of them proved to be essentially as good emitters as the mineral leucite. The fact that all of them melt at temperatures considerably below the melting point of platinum make them superior to leucite, whose melting point is so near that of platinum that melting of the platinum filament often accidentally occurred in fusing the leucite to the filament. It was possible to find examples of all geologic ages among these minerals.

Preliminary experiments with leucite and perthite showed that the *comparison* of the potassium isotope ratio of different specimens with the present apparatus could be made with errors not exceeding 1 percent. It was decided, therefore, to turn to some material whose potassium ratio was thought to vary more than this amount and carry on an intensive study of that material. The kelps of the Pacific were studied, since variations of some 6 percent were reported by Brewer to be customary⁹ and variations up to 15 percent had been claimed.¹⁰

The kelp specimens were collected and dried at room temperature. No chemicals were added to

⁶ J. P. Blewett and E. J. Jones, Phys. Rev. 50, 464 (1936).

⁷ A. K. Brewer, see reference 4.

⁸ Orthoclase and muscovite were originally tried at the suggestion of Professor Bowen.

⁹ A. K. Brewer, Ind. and Eng. Chem. 30, 896 (1938).

¹⁰ A. K. Brewer, J. Am. Chem. Soc. 58, 365 (1936).

contaminate them. They were then cut into small pieces and burned to an ash in a clean, open platinum crucible.¹¹ Enough kelp was used to form about 0.5 g of the ash for each specimen. A brief examination of the kelp ash of *Macrocystis* was made with the aid of a petrographic microscope and standard oils for determining index of refraction. Among the various crystals present, potassium chloride was dominant and potassium sulfate was a minor constituent.¹² Stewart's¹³ thorough examination of the chemical composition of three of the most common Pacific kelps, *Macrocystis pyrifera*, *Nereocystis leutkeana*, and *Pelagophycus porra*, led him to conclude that 85 percent by weight of the total ash is water-soluble, and that of this water-soluble part, 75 percent consists of potassium salts, chiefly potassium chloride and potassium sulfate. His report indicates that the element potassium is present in the ash of these kelps to the extent of about 30 percent by weight. As shown by the exhaustive treatments of the chemical composition of Pacific kelps by Burd,¹⁴ Balch,¹⁵ and Turrentine,¹⁶ the potassium content in some kelps varies considerably from this figure; but by and large, 30 percent may be taken as an average value for the potassium content in the ash of Pacific kelps.

The extensive work by Bondy and his collaborators¹⁷ on hot-filament ion sources showed that chlorides and sulfates of the alkali metals are not desirable to use as ion-emitters because they volatilize so easily that the vacuum becomes bad even at very low temperatures of the filament. Furthermore, the rapid volatilization of the salts readily impoverishes the source of potassium and renders it useless as an ion-emitter after only a short time of heating. For these reasons, Bondy turned to glasses in which various compounds of the alkali metals were incorporated chemically into the aluminosilicate lattice.

¹¹ The platinum crucibles were always cleaned by (1) fusing 10 min. with sodium carbonate, (2) dissolving this away with dilute hydrochloric acid, and (3) heating the crucible for 10 min. at a white heat over a high temperature gas burner.

¹² Personal communication from Professor N. L. Bowen.

¹³ G. R. Stewart, *J. Agr. Research* **4**, 21 (1915).

¹⁴ J. S. Burd, *Calif. Agr. Exp. Sta. Bull.* **248**, 183 (1915).

¹⁵ D. M. Balch, *Ind. and Eng. Chem.* **1**, 777 (1909).

¹⁶ J. W. Turrentine, *Ind. and Eng. Chem.* **4**, 431 (1921).

¹⁷ H. Bondy, G. Johannsen, and K. Popper, *Zeits. f. Physik* **95**, 46 (1935); H. Bondy and V. Vanicek, *Zeits. f. Physik* **101**, 186 (1939).

For the present investigation it was therefore decided that, just as Bondy had done in the case of potassium hydroxide, potassium chloride could be used in preparing an aluminosilicate glass. Using as a guide the ternary system NaAlSiO_4 - KAlSiO_4 - SiO_2 , which was investigated by Schairer and Bowen,¹⁸ it was found that a glass of the approximate composition 57 percent (by weight) KAlSiO_4 , 26 percent NaAlSiO_4 , 17 percent SiO_2 could be made by fusing 0.10 g KCl, 0.05 g NaCl, 0.11 g Al_2O_3 , and 0.18 g SiO_2 in a furnace at 1450°C.¹⁹ An estimation of the relative amounts of kelp ash, Al_2O_3 , and SiO_2 that would be mixed together to give a glass of a composition similar to that above was then made. In calculating the amount of the oxides formed from the alkalis in the chemical reaction of the chlorides and sulfates in the kelp ash with the alumina and silica (and also the oxygen in the air), it was assumed that potassium and sodium are present in kelp ash to the extent of 30 percent and 10 percent, respectively, and that calcium and magnesium together constitute 7 percent of the ash.²⁰ The chlorine, which in the kelp is in chemical union with the alkalis, was liberated in the reaction that formed the alkali aluminosilicates. In making a glass from the kelp ash the actual amounts used for each specimen were: 0.08 g of kelp ash; 0.06 g Al_2O_3 ; and 0.11 g SiO_2 . Since the exact chemical composition of each kelp specimen was not available, these amounts were not critical.

Each mixture was thoroughly stirred in an agate mortar and then heated in a clean platinum crucible in a furnace at 1450°C. The melting point of essentially all of the glasses made was between 1300° and 1400°C. The furnace used was similar to those employed in the Geophysical Laboratories in Washington, D. C. The mixture was heated 20 minutes to permit the complete liberation of chlorine gas and also to assure a rather uniform mixture of the constituents. The crucible holding the melt was then quenched in water to give the glass, which, after being powdered, was applied directly to the filament in the manner previously described. As pointed out

¹⁸ N. L. Bowen, *Am. J. Sci.* **33**, 11 (1937).

¹⁹ The sodium compound was included in order to make a glass of much lower melting point than would result if the sodium were not present.

²⁰ Calcium and magnesium were neglected in writing the above formula but were reckoned into the detailed computations that were made.

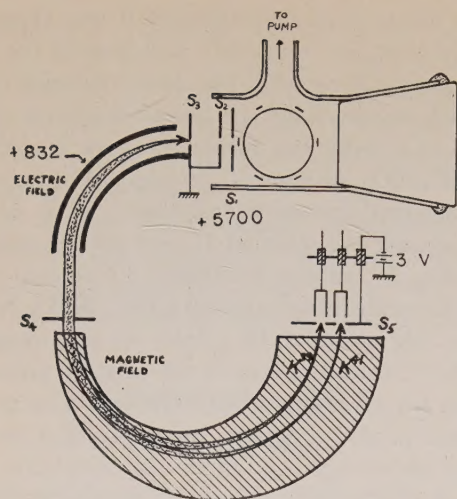


FIG. 1. Arrangement of rotating filament mechanism and collecting unit used on the Dempster double focusing mass spectrograph.

by Blewett and Jones,²¹ the repeated vitrification technique used in phase diagram studies is not necessary for such isotope work.

II. The Apparatus

A. The Mass Spectrograph

In the present investigation Professor Dempster's mass spectrograph of the double focusing type, which has already been completely described by him,²² was used (see Fig. 1). The potassium ions after emission from the hot filament passed through a circular hole of 1-mm diameter in the diaphragm. The diaphragm was at a high potential equal to that of the filament itself and was situated 2 mm from the heated filament. The ions were then accelerated a distance of 7 mm before entering the collimating slit system. Collimation was effected by two slits, the first being $\frac{3}{4}$ mm in width and located 9 mm from the filament and the second being $\frac{1}{2}$ mm in width and located 29 mm from the filament. After passing through the collimating system, the ions were deflected 90° during their passage through the electrostatic field, supplied by two quadrant condenser plates, and then bent 180° in the magnetic field. Upon leaving the magnetic field, the two distinct beams of the K^{39} and K^{41} isotopes were separated by a distance of $4\frac{3}{4}$ mm between the

centers of the respective beams. The width of each beam at this point was found from photographs to be about 1 mm. Each kind of potassium ions then passed through a slit in the collecting unit and entered a separate Faraday chamber. Its arrival was registered by a quadrant electrometer.

The thermionic ion current coming off the filament was of the order of 10^{-6} amp. The potassium ion current entering the collector was between 5×10^{-10} and 5×10^{-11} amp. No trouble with Ca^{40} ions was experienced with the filament temperatures employed.

B. Current and Voltage Sources

The source of the heating current was the $\frac{1}{2}$ -volt secondary of a step-down transformer. The accelerating potential of 5700 volts, which was used throughout the present investigation, was obtained from a transformer and rectified by a kenotron and condenser. An electrostatic deflecting potential of 832 volts was supplied by B-batteries. A 2-microfarad condenser was connected across the charged plates. The magnetic field of 7300–7700 oersteds necessitated a current of 4.15–4.65 amp., which was obtained from lead storage cells. An electromagnet, which was used to compensate for the stray magnetic field in the region of the plates, almost completely prevented any pre-separation of the isotopes before they reached the magnetic field.

C. The Collecting Unit

The slit system in the collecting unit consisted of two 3-mm-wide slits whose centers were placed $4\frac{3}{4}$ mm apart (see Fig. 1). The slits were cut in a $1'' \times 1''$ phosphorbronze plate, which was placed 8 mm above the edge of the magnetic field—this distance being necessarily chosen in order to leave room for the insertion of a photographic plate for supplementary photographic determinations. The phosphorbronze plate was kept at a potential of 3 volts below ground (the cathode was at ground potential) to mitigate effects caused by secondary electron emission. The open end of each Faraday chamber was 1 mm above the phosphorbronze plate. Each chamber was made of 0.005-inch Nichrome foil and was $12 \times 8 \times 3.15$ mm in size. Each was made rather deep to help nullify effects from secondary emission in that most of

²¹ J. P. Blewett and E. J. Jones, reference 6.

²² A. J. Dempster, Proc. Am. Phil. Soc. 75, 762 (1935).

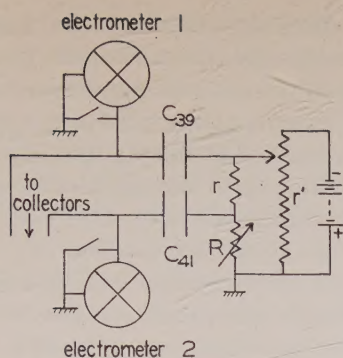


FIG. 2. Circuit used in the null method for measuring the K^{39} and K^{41} ion currents received by the two collectors.

the secondary electrons formed with the chamber would, in the presence of the stray magnetic field, be bent back to the inner sides of the chamber. It was found that the deep collectors alone, without the additional benefit provided by the phosphorbronze plate at a negative potential, were not adequate insurance against noticeable secondary electron effects. By means of Nichrome wire and nickel strips, the plate and collecting chambers were rigidly fastened to three $\frac{3}{16}$ -inch brass rods which passed through amber bushings to the outside of the apparatus. From here electric contact with the electrometers was made through polystyrene-insulated, coaxial cable.

D. The Electrometer Circuit and Null Method

A null method was employed to measure the number of ions entering each collector. The method is identical with that developed by V. A. Bailey²³ and Vanderberg,²⁴ and employed in mass spectrograph work by Straus²⁵ and Sherwin and Dempster.²⁶ Each collector is connected to an electrometer and to one side of a condenser whose other plate is connected to a source of potential, as in Fig. 2. As the charge due to the incoming ions accumulates, the two electrometers are kept at approximately zero potential by adjusting potentiometer r' , it having been previously observed what approximate values to use for r and R . After sufficient charge has been collected and the filament current shut off, an exact null reading of the two electrometers is obtained by

adjusting r' and also the dial box R —resistance r being a dial box maintained at 4000 ohms.

The ratio of the charges on the two systems, and hence of the relative abundance of the isotopes coming in, is given by

$$\text{Ratio of } K^{39}/K^{41} = Q_{39}/Q_{41} = k(R+r)/R. \quad (1)$$

Here $k = C_{39}/C_{41}$ and was 1.298, as determined by capacity bridge measurement. Since r is held constant, it is seen that

$$K^{39}/K^{41} = 1.298(R+4000)/R. \quad (2)$$

Thus, by drawing a curve of K^{39}/K^{41} vs. R , one can readily translate the measured value of R into a measure of the relative abundance of the isotopes.

An electrometer of the Dolezalek type registered the arrival of the K^{39} ions; that registering K^{41} ions was of the Compton type. The Dolezalek instrument had by far the longer period of the two, and it proved advantageous to use it to collect the more abundant K^{39} ions.

E. Comparisons by Rotating Filaments

In the preliminary work on leucite, only one filament at a time was put into the apparatus. It was observed that the same leucite specimen, when left in the apparatus overnight, might show a different K^{39}/K^{41} ratio by as much as 2.5 percent the following day. Sometimes, but not usually, the isotope ratio observed in the afternoon would differ from that in the evening by as great a percentage. These changes were observed in spite of the fact that, insofar as could be detected, all operative conditions were identical. During the course of about one-half hour of making measurements, the ratio usually remained constant within one percent.

These results indicated that in order to compare the isotope ratio of two specimens with an accuracy within 1 percent, it was imperative that they be examined in turn within the time that the same experimental conditions prevailed. A two-electrode arrangement was therefore employed in which the two sources to be compared could alternately be brought in front of the first slit. This arrangement was not entirely satisfactory because the design necessitated that both filaments be heated at the same time. Though they were separated by a distance of 1 cm from each

²³ V. A. Bailey, *Phil. Mag.* **50**, 381 (1929).

²⁴ R. M. Vanderberg, *Phys. Rev.* **59**, 114A (1941).

²⁵ H. A. Straus, *Phys. Rev.* **59**, 430 (1941).

²⁶ C. W. Sherwin and A. J. Dempster, *Phys. Rev.* **59**, 114 (1941).

other, it was observed that the heated filament which was not in front of the slit, would, nevertheless, contribute some of its ions in addition to those from the heated filament that was at the moment under study and directly in front of the slit.

The above results demonstrated the need for a rotating-filament device which would permit two or more specimens to be examined in turn under essentially identical experimental conditions and allow only one filament to be heated at any one time.

F. Mechanism for Rotating Filaments

The rotating-filament device was comprised of three main units: (1) the unit holding the filaments; (2) the brass plate; and (3) the Wilson seal.²⁷ (See Fig. 3.)

The unit holding the filaments consisted of a central $\frac{1}{8}$ -inch brass shaft to which was attached six pure nickel wires (0.040-in. diam.) which radiated out from the shaft at angles of 60° from each other in the form of spokes of a wheel. The six wires were soldered into small holes in the shaft at $\frac{1}{16}$ -in. intervals and were bent so that their ends, which in each case supported one end of the six platinum filaments, fell in the plane of a circle perpendicular to the shaft. Thus each of these six wires, rigidly fixed to the shaft, served to conduct the current to one end of each of the six platinum filaments. Also rigidly affixed to the shaft by means of two nuts and a spring washer, was a Lavite disk.²⁸ Six screws were placed near the outer rim of the Lavite disk at angles of 60° from each other. These screws served two purposes: (1) looped around each screw was a small length of nickel wire which was bent in such a fashion that one end of it could support an end of the platinum filament; (2) the head of each screw was cut down on a lathe to a flat surface, and it served to make electric contact with a contact-screw in the brass plate. Since at a given instant only one of the screws on the Lavite disk was in contact with the contact-screw in the brass plate, only one filament could be heated at any

one time. After the removal of the male part of the ground-glass joint, the complete filament unit could be removed from the apparatus (see Fig. 1). As fresh platinum strips were put onto the filament unit, one end of the platinum filament was soldered to the tip of the nickel-wire spoke, and the other end was soldered to the tip of the nickel wire attached to the Lavite disk.

The brass plate, besides holding the contact-screw already mentioned, carried four screws spaced near the outer rim in such a way that whenever the contact-screw was in contact with a screw on the Lavite disk, they all touched the Lavite disk at points in between the screws in the Lavite disk. In this manner the brass plate resisted the small force offered it by the atmospheric pressure. The side of the brass plate facing the filament unit was counterbored to permit a yoke on the Lavite disk to fit into it. This feature, as well as helping in the alignment of the filament in front of the first slit, also served as an interior support to the filament unit and thus took some strain off the gasket of the Wilson seal. By means of a nickel wire soldered to it, the brass plate supported a circular Nichrome diaphragm ($1\frac{1}{4}$ -in. diam.) in the center of which was cut the first slit.

The Wilson seal was essentially the same as that originally described by Wilson.²⁹ The metal parts of the seal were made of brass. The dimensions used in the single metal part facing the low pressure side were identical to those given in Wilson's paper: the 30° angle was used; since a $\frac{3}{16}$ -in. rod was used, the rubber gasket was made to have an inner diameter of $\frac{3}{32}$ -in. and an outer diameter of $\frac{1}{16}$ -in. The gasket was made with one-sixteenth-in. thick Garlock 353 rubber. In making the metal part on the high pressure side to hold the rubber gasket in place, a simpler design—originally suggested by Mr. Thomas O'Donnell—

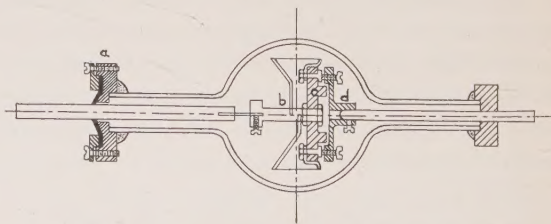


FIG. 3. Rotating filament mechanism.

²⁹ R. A. Wilson, *Rev. Sci. Inst.* 12, 91 (1941).

²⁷ The writer is greatly indebted to Professor Dempster for designing the mechanism for the rotating filaments.

²⁸ Lavite was chosen as the insulating material because it can be easily fashioned to the desired shape on a lathe and then baked in a furnace at $800\text{--}1000^\circ\text{C}$ for a few hours to give a sturdy unit.

was employed. It consisted of one piece of brass fashioned so that the inner circular part fitted down on the gasket while the outer rim rested over the low pressure metal part so that screws could be used to force down the gasket tightly against the latter. The whole Wilson seal unit was held in position by waxing the low-pressure metal part to the extended glass tubing, as shown in Fig. 3. The hole, through which the rod could be either slid or rotated, was drilled slightly large in order to give about $\frac{1}{8}$ -in. freedom of movement of the rod at its end inside the apparatus. This necessary play compensated for the slight discrepancy in the alignment of the two glass tubes inherent in any glass-blown apparatus. The nickel wire, soldered to the end of the rod and made fast to the filament unit by a setscrew, also helped to mitigate this discrepancy by giving the filament unit opportunity to turn so that the face of the Lavite disk would conform to the screws of the fixed brass plate.

RESULTS AND DISCUSSION

I. Observations

To obtain the true value of R and hence the K^{39}/K^{41} ratio (see formula [2]) for any given specimen under study, the two isotope beams were moved across the two collectors by changing the current through the magnet. Figure 4 shows a plot of R against the voltage drop across the magnet obtained in this manner. The curve is characterized by a steep portion to the right, a plateau in the center, a gentle rise toward the left, and then a steep descent to the left. *Before* the central positions are reached by the ion beams as they are being swept, step by step, across the slits, there is an impoverishment of K^{39} ions entering the K^{39} collectors which is reflected

by a higher value for R . In a similar manner—but with opposite results—*after* the central positions are reached by the ion beams and the ions are swept on toward the left (see Fig. 1), there is a diminution of the ions entering the K^{41} collector which is reflected by a lower value of R . These changes are rather critical and therefore cause a sharp rise or fall in the value of R . The gentle rise to the left before it finally drops off steeply is due to the fact that the distance between the edges of the slits in front of the collectors does not exactly conform to the distance between the edges of the two ion beams. During any given run of a specimen at least three, more commonly four, and oftentimes five points would lie along a straight line. Within a single run the points in the plateau region never varied from a straight line by as much as 1 percent of the value of R and usually did not vary by as much as 0.5 percent. A single run thus gave a single value for R and hence of K^{39}/K^{41} .

One of the six specimens was always perthite, which, because of its low melting point, was used as a control sample in preference to leucite. After a run had been made with the control sample perthite, subsequent runs were made on each of the other five specimens of the rotating filament unit. Checks back to the control sample were made frequently. Since each run took about seven minutes, two or three runs on each of the six specimens could be made in one and one-half hours. Such a group of observations over a $1\frac{1}{2}$ -hour period comprises what will be called in this paper a series of runs. After a separate series of runs had been taken, it would generally be followed by one or two subsequent series taken at daily or half-day intervals on the same group of specimens. Then six new filaments were introduced.

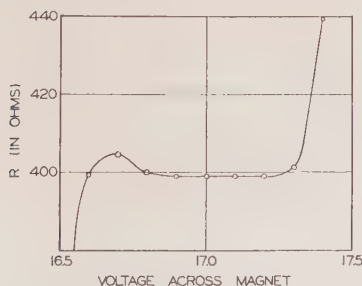


FIG. 4. Curve obtained for a single run.

II. Discussion of Tables

Table I gives the names and sources of the specimens examined in the manner just described. Each specimen is assigned a definite number which is used to identify that same specimen in the subsequent tables. Specimens 36 and 3 to 12 are Pacific kelps; specimens 13, 28, and 37 are fossils; the remaining specimens are rocks. In the footnotes incident to this table are given the

TABLE I. Names of kelp, fossil, and rock specimens and their sources.

Number	Specimen and Source	Number	Specimen and Source
1	Perthite A (control sample) ¹ Lab. specimen, locality unknown	23	Plagioclase feldspar A ^{19,20} Wm. Elliot dike, Butt Tp., Nipissing Dist., Ont.
2	Leucite A ² Civita Castellena, Italy	24	Perthite ^{19,21} Villeneuve Tp., Papineau Co., Que.
3	<i>Pelagophycus porra</i> ³ (kelp) La Jolla, Calif.	25	Green microcline ^{19,22} Lyndoch Tp., Renfrew Co., Ont.
4	<i>Laminaria andersonii</i> stipe ⁴ (kelp) Pacific coast	26	Perthite D ^{23,24} Pied des Monts, Charlevoix Co., Que.
5	<i>Macrocystis pyrifera</i> A ³ (kelp) La Jolla, Calif.	27	Perthite E ^{23,25} Henvey Tp., concession B, lot 5, Parry Sound Dist., Ont.
6	<i>Egregia laevigata</i> ³ (kelp) La Jolla, Calif.	28	<i>Cryptozoon undulatum</i> Bassler B ²⁶ (fossil) 2½ mi. E. of East Galway, Saratoga quadrangle, N. Y.
7	<i>Nereocystis leutkeana</i> stipe A ⁴ (kelp) Pacific coast	29	Perthite F ^{23,27} Monteaige Tp., conc. VII, lot 18, Hastings Co., Ont.
8	<i>Nereocystis leutkeana</i> fronds B ⁵ (kelp) Friday Harbor, Wash.	30	Plagioclase feldspar B ^{23,28} West Portland Tp., range V, lot 2, Lièvre river section of Quebec
9	<i>Pterygophora californica</i> ³ (kelp) La Jolla, Calif.	31	Microcline-perthite G ^{19,29} Mattawan Tp., Nipissing Dist., Ont.
10	<i>Eisenia arborea</i> ³ (kelp) La Jolla, Calif.	32	Perthite H ^{19,30} March Tp., Carleton Co., Ont.
11	<i>Nereocystis leutkeana</i> stipe C ⁶ (kelp) Friday Harbor, Wash.	33	Microcline-perthite J ³¹ Whiteface Mt., Essex Co., N. Y.
12	<i>Nereocystis leutkeana</i> fronds D ⁷ (kelp) Friday Harbor, Wash.	34	Microcline-perthite K ³¹ Whiteface Mt., Essex Co., N. Y.
13	<i>Cryptozoon proliferum</i> Hall A ⁸ (fossil) Saratoga County, N. Y.	35	Perthite L ^{23,32} Huron claim, Winnipeg River, S. E., Manitoba, Canada
14	Chelmsford granite A, ^{9,10} N. Chelmsford, Mass.	36	<i>Macrocystis</i> stipe B ³³ Pacific coast
15	Columbia River basalt ^{9,11} Western part of U. S.	37	<i>Cryptozoon proliferum</i> Hall C ²⁸ Ritchie Park, Saratoga, N. Y.
16	Triassic diabase ^{9,12} Centerville, Va.		
17	Muscovite A ¹³ Ingersoll mine, Keystone, S. Dakota		
18	Muscovite B ¹⁴ Mt. Mica, Paris, Me.		
19	Microcline-antiperthite B ¹⁵ Wilberforce, Ont.		
20	Milford granite B ^{9,16} Milford, Mass.		
21	Leucite B ¹⁷ Mt. Miken, Central Africa		
22	Muscovite C ¹⁸ Spruce Pine, N. C.		

¹ From collection at Rosenwald Museum, University of Chicago. Gift of Professor D. J. Fisher.

² From Ward collection. Gift of Professor D. J. Fisher.

³ Collected Jan. 26, 1943, by Dr. J. F. Wahnus, of the Scripps Institution of Oceanography.

⁴ Secured from California Botanical Material Company, Palo Alto, California.

⁵ Collected Feb. 20, 1938, by Professor G. B. Rigg, of the Oceanographic Laboratories of the University of Washington.

⁶ Collected Dec. 16, 1937, by Professor Rigg.

⁷ Collected in August, 1935, by Professor Rigg.

⁸ Obtained through M. S. Chappars from collection at Walker Museum, University of Chicago. H. P. Cushing and R. Ruedemann, N. Y. State Museum Bull. 169, 38 (1914).

⁹ One of the standard specimens of the Committee on Standards of Radioactivity of the National Research Council being used for the international intercalibration of radioactivity measurements. Gift of Dr. Clark Goodman.

¹⁰ Age: possibly Mississippian. R. D. Evans *et al.*, "Progress Report of National Research Council Committee of Standards of Radioactivity," p. 97. (Mimeographed.) B. K. Emerson, U. S. Geol. Survey Bull. 597, 188 (1917). C. Goodman and R. D. Evans, Bull. Geol. Soc. Am. 52, 491 (1941).

¹¹ Age: Middle Miocene. Evans *et al.*, reference 10, p. 99. R. D. Evans and C. Goodman, Bull. Geol. Soc. Am. 52, 483 (1941).

¹² Age: Triassic. Evans *et al.*, reference 10, p. 95.

¹³ Age: Early pre-Cambrian, about 1465 million years old. Collected in summer of 1943 by Professor D. J. Fisher. Occurred in same pegmatites as those from which radioactive determinations of age have been made. A. F. Kovarik, Am. J. Sci. 20, 81 (1930). A. Holmes, "Age of the Earth," Nat. Res. Council Bull. 80, p. 338.

¹⁴ Age: Late Silurian or Devonian. Obtained through Professor E. S. Bastin from collection of Rosenwald Museum, University of Chicago. E. S. Bastin, U. S. Geol. Survey Bull. 445, 15 (1911).

¹⁵ Age: Middle pre-Cambrian. Gift of Professor Harry Berman. Holmes, reference 13, p. 325. H. V. Ellsworth, Econ. Geology Series No. 11, Geol. Survey, Canada, p. 54 (1932). H. S. Spence and R. K. Carnochan, Canadian Institute of Mining and Metallurgy Bulletin, pp. 1-37 (1930).

¹⁶ Age: Devonian (?). Emerson, reference 10, p. 165.

¹⁷ Age: Probably recent though perhaps Tertiary. Gift of Professor Bowen. N. L. Bowen and R. B. Ellestad, Am. Mineral. 22, 410 (1937).

¹⁸ Age: late Carboniferous or early Permian (?). From a pegmatite specimen containing much altered uranium material. Gift of Professor Berman. Holmes, reference 13, pp. 340 ff.

¹⁹ Age: Middle pre-Cambrian. Gift of Dr. H. V. Ellsworth.

²⁰ Ellsworth, reference 15, p. 188.

²¹ Reference 15, p. 242.

²² Reference 15, p. 228.

²³ Age: Middle pre-Cambrian. Gift of H. S. Spence.

²⁴ Associated with uraninite, thucholite, etc. H. S. Spence, Am. Mineral. 25, 711 (1940).

²⁵ Associated with uraninite, thucholite, etc. H. S. Spence, Am. Mineral. 15, 499 (1930). H. V. Ellsworth, Am. Mineral. 16, 576 (1931).

²⁶ Age: Upper Cambrian. Obtained through Dr. Winifred Goldring, N. Y. State Paleontologist, as a gift from the N. Y. State Museum.

²⁷ Associated with ellsworthite, thorite, etc. H. V. Ellsworth, Am. Mineral. 12, 368 (1927). T. L. Walker and A. L. Parsons, Univ. Toronto Studies 16, 13 (1923).

²⁸ Associated with monazite. H. S. Spence and O. B. Muench, Am. Mineral. 20, 726 (1935).

²⁹ Ellsworth, Econ. Geol. Series No. 11, p. 190.

³⁰ Reference 29, p. 238.

³¹ Age: Middle pre-Cambrian, 1200 million years old. Associated with allanite. Gift of Dr. Marble. J. P. Marble, Am. J. Sci. 241, 32 (1943).

³² J. S. DeLury and H. V. Ellsworth, Am. Mineral. 16, 569 (1931).

³³ Secured from General Biological Supply House, Chicago, Illinois.

names of the donors of the specimens, the ages of the specimens whenever known, and references which give the geologic occurrence of the rock specimens. The species of kelp examined include the most common ones of the Pacific coast. The fossil specimens examined are the same species as those previously investigated by Brewer and Baudisch.³⁰ Most of the rock specimens examined

came from well-known localities and were once a part of pegmatites whose ages have been relatively well established not only by geologic evidence, but also by radioactive age determinations.

Tables IIA, IIB, and IIC give the values of the potassium isotope ratio obtained from the various specimens. A condensed form of the full name of the specimens occurring in Table I is given in these tables (in column 2) to facilitate interpretation of them. Within each individual vertical

³⁰ A. K. Brewer and O. Baudisch, J. Am. Chem. Soc. 59, 1578 (1937).

TABLE IIA. K^{39}/K^{41} isotope ratios for kelp, fossil, and rock specimens.

Number	Specimen	1	2A	2B	2C	3A	3B	3C	4A	4B	5A	5B
1	Perthite A	14.21(3)	14.03(3)	14.34(4)	14.25(2)	14.19(3)	14.29(4)	14.40(2)	14.33(3)	14.36(5)	14.33(4)	14.40(4)
2	Leucite A		14.00(3)	14.31(1)	14.28(1)							
3	Pelagophycus	14.22(2)	14.00(2)	14.40(2)	14.28(2)						14.40(4)	14.40(2)
4	Laminaria	14.19(2)							14.34(2)	14.31(2)		
5	Macrocystis		13.97(2)	14.38(2)	14.34(2)				14.33(2)	14.37(1)	14.31(2)	14.46(2)
6	Egregia		13.97(2)	14.37(1)	14.31(1)				14.34(2)	14.34(2)		
7	Nereocystis A		14.09(1)	14.44(3)	14.28(2)							
8	Nereocystis B					14.12(1)	14.22(2)	14.42(1)				
9	Pterygophora					14.15(1)		14.37(1)	14.37(2)	14.42(2)		
10	Eisenia					14.12(1)	14.25(2)	14.36(2)			14.28(2)	14.44(2)
11	Nereocystis C					14.28(1)	14.22(2)	14.48(1)			14.36(3)	14.37(3)
12	Nereocystis D								14.37(2)	14.36(2)		
14	Granite A					14.19(1)	14.28(1)	14.40(1)				
	Average ...	14.21	14.01	14.37	14.29	14.18	14.25	14.41	14.35	14.36	14.33	14.41

TABLE IIB. K^{39}/K^{41} isotope ratios for kelp, fossil, and rock specimens.

Number	Specimen	6A	6B	7A	7B	8A	8B	8C
13	Cryptozoön A	14.25(2)	14.46(3)			14.44(1)	14.28(4)	14.22(1)
14	Granite A			14.54(2)	14.63(2)			
15	Basalt	14.31(3)	14.49(3)			14.58(1)	14.43(2)	14.34(1)
16	Diabase	14.27(2)	14.48(2)			14.44(1)	14.37(2)	14.28(1)
17	Muscovite A	14.28(2)	14.51(2)			14.58(1)	14.43(2)	14.28(1)
1	Perthite A	14.27(4)	14.50(4)	14.58(4)	14.68(3)	14.57(2)	14.43(4)	14.33(2)
18	Muscovite B	14.28(2)	14.51(2)			14.58(1)	14.44(2)	14.33(1)
19	Perthite B			14.57(3)	15.51(4)			
20	Granite B			14.51(2)	14.54(2)			
21	Leucite B			14.53(2)	14.58(2)			
22	Muscovite C			14.53(2)	14.51(3)			
	Average	14.28	14.49	14.54	14.58	14.54	14.40	14.30

TABLE IIC. K^{39}/K^{41} isotope ratios for kelp, fossil, and rock specimens.

Number	Specimen	9A	9B	9C	10	11A	11B	12
3	Pelagophycus	14.28(2)	14.63(2)	14.25(1)				
5	Macrocystis	14.27(1)	14.68(1)	14.31(1)				
6	Egregia				14.30(3)			
7	Nereocystis A				14.40(1)			
10	Eisenia				14.44(1)			
23	Feldspar A	14.22(1)		14.28(2)				
24	Perthite C	14.27(1)		14.25(1)				
25	Microcline	14.31(1)		14.34(1)				
1	Perthite A	14.27(3)	14.70(2)	14.28(3)	14.37(4)	14.18(3)	14.32(3)	14.57(5)
26	Perthite D				14.34(1)			
27	Perthite E				14.37(1)			
28	Cryptozoön B						14.21(3)	
29	Perthite F					14.25(1)	14.34(1)	
30	Feldspar B					14.15(1)	14.34(1)	
31	Perthite G					14.15(1)	14.31(1)	
32	Perthite H							14.58(2)
33	Perthite J							14.51(2)
34	Perthite K							14.46(2)
35	Perthite L							14.48(2)
	Average	14.27	14.67	14.29	14.37	14.18	14.31	14.52

column headed by the series number there customarily appear six values—in a few instances there are less than six—which are the isotope ratios of the six specimens used in that series of runs. The number in parenthesis indicates the number of runs made on that individual specimen during the series. The value for the ratio given for any individual specimen is the arithmetic

mean of the values obtained on the specimen for that given number of runs. At the bottom of each vertical column appears a number which is the average of the series of runs of the six specimens.

Examination of the data reveals that *within a single series of runs* the largest value for the mean isotope ratio does not ordinarily differ from the smallest value by more than 1 percent. Within

three different series (3A, 5A, and 7B), however, are found differences greater than 1 percent, yet smaller than 1.3 percent. It should be emphasized that these figures do not do justice to the degree of accuracy that was obtained insofar as a direct comparison between the isotope ratio of the specimens is concerned. For during the time of making a series of runs, slight fluctuations were observed (these fluctuations will be discussed presently) and are reflected in these figures. By interchecking the specimens with the control sample at the proper time, readings with an average deviation of a single observation of about ± 0.04 for the K^{39}/K^{41} ratio could be attained. Thus the accuracy in comparing the isotope ratio of any six specimens was well within 1 percent—perhaps within 0.5 percent. Within this accuracy, the relative abundance of isotopes in all the specimens examined—whether they were kelp-glasses, fossils, or rocks of different geologic age—never varied from that of the control sample.

Though the potassium isotope ratio within any series of runs was constant within experimental error, there were noted definite fluctuations of the ratio under different conditions of the apparatus or of the emitters on different days. Usually the series of runs here presented were made at approximately daily intervals. When, after a one-day interval, a subsequent series of runs was taken on the same six specimens, the isotope

TABLE III. K^{39}/K^{41} isotope ratios for specimens used in the preliminary work.

Fil. No.	Day*	Specimens		Fil. No.	Day	Specimen
		Leucite A	Macrocyctis B			Leucite A
1		13.60(2)	13.53(5)	5		14.06(4)
2	1A	14.15(9)	14.05(3)			Leucite B
	1B	13.91(7)	13.78(5)	6	1	13.66(3)
	23	13.91(2)	13.75(3)		2A	14.03(5)
	24	13.96(5)	13.96(4)		2B	13.94(3)
	26	14.06(6)	14.03(4)		3A	14.12(3)
	27	14.06(4)	14.06(3)		3B	14.12(3)
	28	14.06(2)	14.06(7)		4	14.25(3)
			Perthite A		5A	14.28(3)
3	1A	14.31(7)	14.28(3)		5B	14.28(3)
	1B	14.22(4)	14.22(2)		6A	14.22(3)
	7A	..	14.38(3)		6B	14.09(3)
	7B	..	14.00(2)		7A	14.22(3)
	8	..	13.91(3)		7B	14.22(3)
			Leucite B			Macrocyctis B
4	1A	13.78(3)	13.78(6)	7	1	13.44(1)
	1B	13.87(2)	13.81(5)		2	13.46(4)
				8		14.33(3)
Specimen		Ratio		Specimen		Ratio
Cryptozoon A		13.59(2)		Laminaria		13.59(3)
		13.67(3)				
Nereocystis A		13.63(3)		Pelagophycus		14.51(3)

* A means afternoon; B, evening.

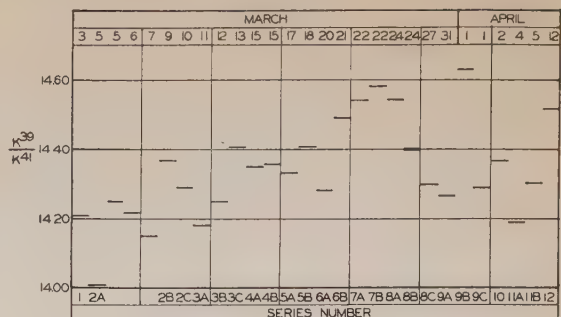


FIG. 5. Comparison of values of the K^{39}/K^{41} isotope ratio taken over a period of six weeks.

ratios of all specimens would not vary from each other by more than 1 percent, yet the ratio now observed might differ by as much as 3 percent from its value the preceding day. During the interim the vacuum was never broken although the pumps were always shut off and the pressure went up to about 10^{-3} mm during the night. After breaking the vacuum and introducing six fresh platinum filaments with glasses fused onto them, the isotope ratio of the six new specimens would not vary from each other by more than 1 percent, yet it might differ by as much as 2 percent from that of the previous series. Figure 5 shows how the ratios varied with the different series of runs taken over a period of about six weeks. Series 1 through 8B were made regularly at almost daily intervals over a period of three weeks. These series appear to exhibit a trend of an increase in the isotope ratio during the three-weeks period. After series 8B was made, three days elapsed, during which the pressure in the apparatus was 10^{-3} mm of mercury. Series 8C was then obtained, after which the apparatus stood at a pressure of 10^{-3} mm for three more days before the new specimens on which series 9A was made was put into the apparatus.

It is interesting to note that in one isolated case the conditions suddenly changed so that a large fluctuation was witnessed during one series of runs (9B). Before the writer had time to complete this series the ratio abruptly changed from a value of about 14.63 to about 14.29. Accordingly, the remainder of the determinations on that day were treated as a separate series, namely 9C, inasmuch as it was apparent that whatever caused the fluctuations had instantaneously appeared here. It should be emphasized

that in this instance the isotope ratio of all the specimens spontaneously changed. This case was the only observed example of such a large fluctuation occurring within a series of runs at the time of observation.

Three consecutive series of runs, which were purposely left out of Table II to help condense it, were made between series 2A and 2B on the specimen Perthite A only. The values of the isotope ratio obtained, in proper order, were 14.25 (7), 14.22 (3), 14.15 (5), and are included in Fig. 5 for completeness.

One part of the fossil *Cryptozoön C* (specimen 37) was included in series of runs 11A and 11B, and another part of the same fossil was included in series 12. No measurable ion current was registered, however, this fact probably being due to excessive leaching of the specimen. Satisfactory potassium ion emission was obtained from two fossil specimens, *Cryptozoön proliferum* Hall A and *Cryptozoön undulatum* Bassler B, by merely powdering the specimens and putting them on the filaments in the usual manner. Within the 1 percent accuracy obtainable, the isotope ratio of both fossils was found to be the same as that of the rock control sample. These results on the fossils do not agree with those of Brewer and Baudisch,³⁰ who reported—for the same species—*isotope ratios lying about 2 percent below Brewer's normal value of 14.20 to 14.25.*

It is noteworthy that in the preliminary investigations, before the rotating filament mechanism and Wilson seal were introduced into the apparatus, somewhat lower values of the isotope ratio than those presented in the above tables were generally observed. Table III gives the observed ratios in this preliminary work. Those specimens bearing the same filament number in the table were placed together in the apparatus when the two-filament mechanism was used. All other specimens in the table were placed alone into the apparatus.

If we give each series of runs in Tables IIA, IIB, and IIC equal weight, the arithmetic mean of the values of the isotope ratio is 14.35. Similarly the arithmetic mean of the values in Table III is 13.88. An average of these two figures, considering them of equal weight, gives 14.12 as a kind of "average" isotope ratio for all the runs made. In this case, the "average" is

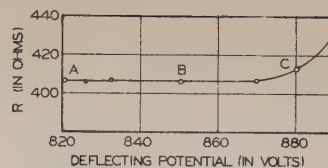


FIG. 6. Effect of changes in deflection potential upon resistance R .

rather meaningless except insofar as it helps to give a notion of the absolute value of the isotope ratio. The writer is of the opinion that the value 14.12 is within 2 percent of being the correct absolute value of the potassium isotope ratio. This result is in good agreement with that of Brewer, who gives 14.20 to 14.25 as the normal ratio.³¹

The surprisingly small amount of potassium that is apparently necessary in the crystal lattice of a mineral to yield a satisfactory ion current is worthy of comment from a petrographic standpoint. Specimen 19, consisting of dominant plagioclase feldspar and only a very minor amount of microcline, was a satisfactory emitter of potassium ions. Specimens 23 and 30 were lacking in any visible potash mineral and were comprised wholly of plagioclase insofar as could be determined with the aid of a petrographic microscope. Yet they proved to be good potassium ion-emitters. The explanation is that some potassium ions, in spite of their difference in size from sodium and calcium ions, have gone into the crystal lattice of the plagioclase to form a mixed crystal. Heating the crystal sets the potassium free.

III. Discussion of Fluctuations

While the fluctuations do not hinder the *comparison* of the isotope ratio of different specimens to within 1 percent error, they nevertheless prevent the attainment of a greater accuracy than about 2 percent for the absolute relative abundance of the isotopes.

A. Possible Causes Inherent in the Apparatus

To show that the fluctuations could not be due to pre-separation of the isotopes due to stray magnetic field, a number of runs were made during which the deflecting potential was changed

³¹ A. K. Brewer, J. Chem. Phys. 4, 350 (1936); J. Am. Chem. Soc. 58, 365 (1936); J. Am. Chem. Soc. 61, 1597 (1939).

(see Fig. 6). The definite up-swing of the curve for the value of R corresponds to a decrease in the K^{39}/K^{41} value. The decrease of isotope ratio in region C of the curve means that the K^{39} ions were the first ones to be cut off by the edge of slits S_4 as the increasing deflecting potential swung the ions around in a path of decreasing radius. There was, therefore, a slight enrichment of the K^{39} ions on the inner edge of the beam coming through the electrostatic deflecting plates. As the ions were swept over to the other side of slit S_4 by decreasing the deflecting potential, a corresponding enrichment of the K^{41} on that side was not reflected in a down-swing of the curve in region A . The electrometers were not sufficiently sensitive to register such a small increase in the K^{41} ions, this increase being only about $1/14$ as great as the increase of K^{39} ions in region C . The wide, level plateau in region B indicates that essentially no pre-separation was present within the main body of the ion beam.

Rather large changes in the current flowing through the two compensating electromagnets failed to give any measurable change in the isotope ratio. Hence, variations of current through these magnets could not have been the cause of the fluctuations.

There is a possibility of a slight pre-analysis effect due to the stray magnetic field over the 29-mm distance that the ions traveled from the filament to the region of compensating field. However, it is impossible that it could produce a large, spontaneous change such as was observed between Series 9B and 9C.

No change in the isotope ratio was observed when the accelerating potential was given a value lying 100 volts on either side of the 5700-volt value that was customarily used. Because the accelerating potential would never by itself vary by as much as 100 volts, its variations are ruled out as a cause of the fluctuations.

Before every series of runs, the two electrometers were always charged and left in this condition for a few minutes to ascertain that there were no measurable leakages over the surface of the amber bushings or in the leads from the apparatus to the electrometers.

Periodic checks of the ratio of the capacity of the two condensers used in the null electrical circuit were made throughout the seven months

of measurements and indicated that the ratio never varied by more than two parts in a thousand from the average value of 1.298. In order to test the leakage from one condenser plate to the other because of ionization in the condensers, those plates leading to the electrometers were grounded while the respective voltages ordinarily used to balance the total number of incoming ions were impressed on the opposite plates; then the electrometers were disconnected from ground and the amount of drift observed. During the 30 seconds of time ordinarily taken for a single reading, the amount of leakage amounted to less than 1 mm scale-deflection of the electrometer from its original position. This small amount is within the limit of accuracy of reading the scale during a run. Hence, variations due to the changing capacities of the condensers or leakage across the condensers could not cause the large fluctuations observed.

The results obtained whenever experiments were tried to determine the effect of a change in pressure on the isotope ratio are insufficient to conclude whether any consistently definite change may indeed exist from this cause. Inasmuch as the main purpose of the present investigation is to compare the ratios among kelps and among rocks of different geologic age, these experiments were treated as incidental, but would have been carried on somewhat further, had not the exigencies of war necessitated bringing this work to a close at the present time. The results of various runs made on successive days on the same specimen do suggest an increase in the isotope ratio—as has already been pointed out. A similar tendency was observed in the preliminary work, as is best exemplified by the series of runs made on Leucite A, Leucite B, and *Macrocystis B* (see Table III). The tendency was not always present, however. Indeed, the isotope ratio of Perthite A, for example, tends to decrease markedly.

It has already been noted that the isotope ratios of the specimens examined in the preliminary work tended to be considerably lower in value than the ratios obtained after the introduction of the Wilson seal. It is believed that the Wilson seal limited the vacuum conditions so that pressures less than 10^{-5} mm of mercury were not attained after its introduction. Because of a faulty relay—which could not be repaired or

replaced at this time—the exact pressure conditions were unfortunately not known during the latter part of the work.

It has been shown by Sherwin³² that the chance of neutralization of a positive ion in passing through a gas depends on the velocity of the ion. As the energy of the two potassium isotopes was the same, the velocity of the lighter isotope is 2.5 percent greater than the heavier isotope and consequently might be weakened by absorption at a different rate from that for the light isotope. Sherwin's results on hydrogen give a change of cross section for neutralization of less than one part in 100 for this difference of velocity. In terms of the original intensity I_0 , the intensity of the bundle after going 60 cm (the approximate distance of travel through the present apparatus) at a pressure of 10^{-4} mm is $I = I_0 e^{-n\sigma \cdot 60}$, where $n = 3.55 \times 10^{12}$ and $\sigma = 0.3 \times 10^{-16}$ cm². Thus

$$I = I_0 \exp [-6 \times 10^{-3}] = I_0 (1 - 6 \times 10^{-3}).$$

Thus the weakening of the potassium ion bundles in the 60 cm used, even at the very high pressure of 10^{-4} mm, would have been less than one percent. Since a difference of one part in 100 in the one percent is far below the possibility of observation, any residual gases are incapable of causing a measurable difference in the isotope ratio due to a difference in rate of neutralization.

B. Causes Inherent in the Emitters

Causes inherent in the emitters offer a likely explanation of the fluctuations. It is conceivable that various hydrocarbons that are always present in the apparatus may form a coating on the filaments and change the ratio of the ions being emitted from the heated glass ion source. In his investigation of the isotope effect in the evaporation of lithium, potassium, and rubidium from thermionic sources over a period of time, Brewer³³ observed a change in the abundance ratio for lithium, but none for potassium or rubidium. In view of the change of the isotope ratio of lithium over a period of time, it seems not unreasonable that under some circumstances there might occur a similar isotope effect with the other alkali metals. With the particular potassium aluminosilicates used in the present investigation, it may

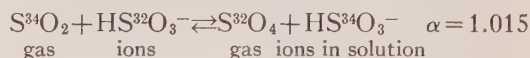
be possible that the potassium experienced such an isotope effect in being emitted from the glasses.

Of all the possible causes for the fluctuations that have been advanced in the above discussion, it seems that the most probable one lies in some kind of surface phenomenon of the emitter—a phenomenon which permits different amounts of the two potassium ions to evaporate at different times.

GEOLOGICAL CONSIDERATIONS AND DISCUSSION

In the laboratory the artificial separation of isotopes can be carried out in many ways. In a search, therefore, for a plant, animal, or rock in which the relative abundance of the isotopes of some element might vary, one logically explores the naturally occurring processes which might conceivably effect the separation of the isotopes in some manner similar to well-established laboratory methods. It is to be emphasized that the requirement of such a process is that it is recurrent or that it comes in cycles, which, given time enough, will effect the separation.

Because there is generally a great degree of physical mixing of all elemental constituents during the *extrusive* manifestations of vulcanism, there is little likelihood that any measurable separation of the isotopes is effected during the formation of extrusive rocks. There is a possibility that the equilibrium³⁴



may be present within molten volcanic lava, yet it is difficult to see how the separation effect could be cumulative enough to make measurable differences in the isotope ratio of the sulfur.

Nor is it probable that the *intrusive*, or *plutonic*, manifestations of vulcanism have effected a measurable separation. Professor Bowen³⁵ has pointed out that in the cooling masses of magma, in order to produce important results in the way of fractional crystallization, the molecular flow of diffusion of substance, which would be selective to the materials participating in it, must play a negligible role in comparison with the factors involving the relative movement of crystals and liquid. He points out that this relative movement

³² C. W. Sherwin, *Phys. Rev.* **57**, 814 (1940).

³³ A. K. Brewer, *J. Chem. Phys.* **4**, 350 (1936).

³⁴ T. I. Taylor, *Science* **89**, 177 (1939).

³⁵ N. L. Bowen, *The Evolution of the Igneous Rocks* (Princeton Press, 1928), p. 22.

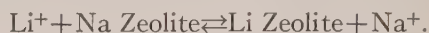
may take place under the influence of gravity during the early stages and under the influence of deformative forces during the middle and late stages of crystallization. The process is probably inadequately cyclic ever to produce a measurable separation by gravitation—even under ideal conditions of crystal settling, when comparatively little movement of the crystals take place. Yet it will be of interest—particularly when more accurate mass spectrographs are built—to investigate those igneous rocks whose formation is ascribed partly to gravitative settling, such as are those from the Sudbury district of Canada³⁶ and the Bushveld Complex of South Africa.³⁷

Mineralizers are those components of magmatic solutions which, because of their low molecular weight, or catalytic action, or for any other reasons, exert a large influence on the other components of the magma. The mineralizers include water, fluorine, boron, and chlorine. It is not known at the present time what physical condition the mineralizers are in when they are most influential, but it is probable that they are partly in the vapor state at the pressure and temperature conditions encountered in contact metamorphism and in the formation of pegmatites. If one of the isotopes of boron or chlorine is more ready to enter into combination than the other isotope, we might expect to find one side of a bed having minerals with more of this isotope than those on the other side.

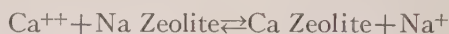
Diastrophism would aid the above-mentioned phases of vulcanism only by forming cracks and other openings through which gases or liquids could flow, and pockets where separation of a very local nature might be carried on. These would be minor and relatively unimportant.

It is the process of gradation that offers the best prospects in a search for a naturally occurring separation of the isotopes by geologic processes. For here lies a number of physical processes which may be adequately recurrent or, because they are operative over great lengths of time or distance, may be very effective. One of these phenomena is base exchange, by means of which certain elements in a mineral may be exchanged or replaced by the ions of other elements

in solution. This type of replacement is very common, particularly in the case of soil formation, and is effected by gradational agents such as ground water, running water in streams, or oceanic waters. The rocks which best exhibit base exchange are zeolitic rocks and clays. Taylor,³⁴ in collaboration with Urey, has already obtained "appreciable changes" in the isotope ratio of lithium by chemical exchange with sodium zeolites which show the following equilibrium:



In this instance one isotope of lithium replaces the sodium in the zeolite better than the other lithium isotope. By allowing a solution of sodium chloride to pass slowly through a 10-cm column of potassium-bearing, zeolitic greensand, Brewer³⁸ found that the greensand was impoverished preferentially of the K³⁹ isotope. He suggests that this effect could occur in nature where base exchange processes are operative. The base exchange taking place in zeolitic rocks is commonly of the type:



in which the calcium ions in solution go into the crystal lattice where the sodium was originally. In the process it is likely that the isotopes of calcium go into the zeolite at slightly different rates. In the event that calcareous ground water were to run for many miles along an aquifer containing porous volcanic material—and hence probably zeolitic rocks—a substantial and possibly measurable separation of the calcium isotopes could be effected. The isotope effect would be one of lateral gradation.

Because clay deposits are more widespread than zeolitic rocks, base exchange in the clays is in some respects more far-reaching than in the zeolites. As pointed out by Kelley,³⁹ there are several elements that can be replaced in the clays, and there is a definite replacing power of the common cations in the order: $\text{Na} < \text{K} < \text{Mg} < \text{Ca} < \text{H}$. Thus, sodium has less replacing power than potassium, potassium less than magnesium, and so forth. In addition—in the case of the bentonite clays, which have the highest base exchange capacity of all the clays—

³⁶ A. P. Coleman, *Econ. Geol.* **19**, 569 (1924).

³⁷ R. A. Daly and G. A. F. Molengraaff, *J. Geol.* **32**, 33 (1924).

³⁸ A. K. Brewer, *J. Am. Chem. Soc.* **61**, 1597 (1939).

³⁹ W. P. Kelley, "Base Exchange in Relation to Sediments," *Recent Marine Sediments* (Thomas Murby and Company, London, 1939), p. 455.

ions of magnesium, iron, or both of these elements in solution may go into the crystal lattice of clay minerals and replace the original aluminum.³⁹ The exchange processes probably proceed at different rates that depend on the isotopes involved. Therefore, ground water which percolates long distances down inclined beds of bentonite in a direction parallel to the bedding may possibly effect a measurable separation of the isotopes of some of the above elements involved in base exchange. The widespread occurrence of bentonite deposits in the western United States makes the possibility of such a separation rather favorable. The separation would be one of lateral gradation; and therefore sampling could be done on the same bed at different localities.

Experiments have as yet been unable to show any isotope separation effect on a column of material migrating through a substance like gelatine.⁴⁰ It has been suggested by Lindemann⁴¹ that the head of the column would be richer in the lighter isotope. If success is ever attained in the laboratory, it would be of interest to investigate diffusion (or Liesegang) banding in rocks for an isotope effect. As demonstrated in the experiments of Liesegang and as explained by Oswald, the phenomenon of diffusion banding in rocks is a solution phenomenon. It is the result of rhythmic supersaturation of a solution permeating through a "solid" or colloidal substance.⁴²

The phenomenon of replacement is so widespread in rocks that it will be well some day to review the whole process in terms of established chemical equilibrium relations.

One can only speculate as to the exact nature of the chemical equilibria that were present in the great inland seas and marine basins of the geologic past. However, the conditions which were influential in forming the great sedimentary salt beds and the limestone beds could not have been greatly unlike those existing on earth today. During the thousands of years of evaporation necessary to produce the thick deposits of salt, there were doubtlessly in operation the processes of free evaporation, ionic migration, gravitative settling, fractional crystallization, and chemical exchange.

⁴⁰ F. W. Aston, *Mass Spectra and Isotopes* (Longmans, Green and Company, New York, 1939), pp. 244-61.

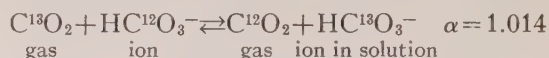
⁴¹ F. A. Lindemann, *Proc. Roy. Soc. A* **99**, 103 (1921).

⁴² E. S. Hedges, *Liesegang Rings and Other Periodic Structures* (Chapman and Hall, Ltd., London, 1932), p. 52.

Robinson and Briscoe⁴³ have shown that in subjecting ammonium bromide to prolonged fractional crystallization involving about 2700 crystallizations, the isotope ratio of the bromine in the "head" fractions did not differ from that in the "tail" fractions by 1 percent. It is probable, therefore, that no measurable separation was effected by fractional crystallization in ancient salt basins.

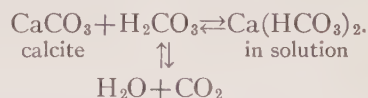
Lewis and Macdonald⁴⁴ have demonstrated the separation effect of lithium amalgam as it passed through a long, narrow column of lithium chloride solution. In this case the lighter lithium isotope was carried down preferentially and accumulated at the foot of the column. It is doubtful that organisms, even in isolated bodies of water, could give the same result as the amalgam with measurable isotope effects.

Just as there exists in the present-day seas the equilibrium



in which the heavier isotope prefers to form the ion,⁴⁴ so within the ancient seas there was probably maintained the same equilibrium. The lime-secreting organisms that used the HCO_3^- ion in their metabolism would, therefore, have their organic parts enriched in C^{13} . If their organic remains later accumulated to form a limestone deposit, this enrichment should be reflected in a lower $\text{C}^{12}/\text{C}^{13}$ isotope ratio for that limestone as compared with other rocks. It is interesting to note that the Grenville limestone examined by Nier and Gulbransen⁴⁵ did indeed show an enrichment of the C^{13} isotope by as much as 3 percent.

Professor Dempster⁴⁶ suggests the possibility of there being a separation effect in the case of long, narrow stalactites. In this case the purely chemical equilibrium (not emphasizing isotopic equilibrium) is as follows:



⁴³ P. L. Robinson and H. V. A. Briscoe, *J. Chem. Soc. London* **127**, 138 (1925).

⁴⁴ G. N. Lewis and R. T. Macdonald, *J. Am. Chem. Soc.* **58**, 2519 (1936).

⁴⁵ Nier and Gulbransen, *J. Am. Chem. Soc.* **61**, 697 (1939).

⁴⁶ Personal communication from Professor Dempster.

The cyclic deposition and redissolving which takes place might tend to leave the heavier calcium isotopes at the top of the stalactite, whereas the lighter ones might preferentially migrate in solution to the bottom and be deposited there. It would be of interest to make isotope determinations on long pencil stalactites in particular.

In this paper the writer has not attempted to discuss the many biological processes which may later be found to offer excellent opportunities for separation of isotopes. Thirty-five years ago Balch⁴⁷ commented on the little-known fact that plants such as kelp, although growing in an oceanic medium where sodium abounds, are nevertheless able to assimilate the much less-abundant potassium to the extent of 30 percent by weight of their ash as compared with 10 percent sodium. It will not be surprising, therefore, if plants and animals are later found to show great preferential assimilation of isotopes as well as of elements. The results of the present investigation indicate, however, that though a plant may show a great preference for an element, it need not show a correspondingly great preference for any individual isotope of that element.

CONCLUSIONS

1. It has been found that the naturally occurring minerals that prove excellent thermionic emitters of potassium ions include orthoclase, microcline, muscovite, perthite, and microcline-perthite. It is believed that further study will show that many other naturally occurring potassium-bearing aluminosilicates are equally good emitters.

2. An examination of the most common Pacific kelps indicates that their potassium isotope ratio does not vary by more than 1 percent from that of rocks. In this respect the writer was unable to verify the results of Brewer.

3. An examination of two species of *Cryptozoön* fossils of Upper Cambrian age shows no difference in their potassium isotope ratio, within 1 percent error, from that of rocks. This result does not agree with that reported by Brewer and Baudisch on the same two species of fossils.

4. An examination of rocks of different geologic

age, from Early pre-Cambrian to Tertiary, shows no measurable change in the potassium isotope ratio within the 1 percent accuracy obtainable.

5. The observed fluctuations of the isotope ratio are apparently due to isotope effects of the ion source.

6. With the laboratory methods of artificial separation of isotopes as a guide, an examination of the geologic processes has been made in an attempt to suggest where further evidence might be found that a measurable isotopic separation has been effected in rocks. Apart from biological processes, the geologic process of gradation appears likely to afford the best physical means of separating isotopes naturally. The phenomenon of base exchange in the zeolites and bentonite clays offers the best possibility of finding a measurable separation.

7. Chemical equilibrium within the ancient seas, coupled with the agency of lime-secreting organisms, may account for the enrichment observed by Nier of Grenville limestone in the C^{18} isotope.

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⁴⁷ Balch, *Ind. and Eng. Chem.* **1**, 777 (1909).

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